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### Abstract

We outline recent progress exploiting neutron reflectivity for structural and compositional investigations of the solid-liquid interface. There has been extensive activity in this area, with key areas of development: (i) an increased range of accessible substrates (e.g. metals and minerals), (ii) novel liquid phases, and (iii) strong themes in electrochemistry (e.g. batteries), corrosion, polymers and increasing application of extreme conditions.

**Keywords** solid-liquid; neutron reflection; interface; electrochemistry; pressure; polymer; corrosion; batteries; supercapacitors; shear; drug delivery; responsive materials

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# New Insights into the Solid-liquid Interface Exploiting Neutron Reflectivity

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## Abstract

We outline recent progress exploiting neutron reflectivity for structural and compositional investigations of the solid-liquid interface. There has been extensive activity in this area, with key areas of development: (i) an increased range of accessible substrates (e.g. metals and minerals), (ii) novel liquid phases, and (iii) strong themes in electrochemistry (e.g. batteries), corrosion, polymers and increasing application of extreme conditions.

## 1 Introduction

This review focusses on studies of the solid-liquid interface using neutron reflectometry (NR), with a particular emphasis on new developments and applications. While concentrating on work in the last 3-4 years alone, we acknowledge that much excellent work cannot be included and in many cases the references given are only representative examples. We also do not attempt to cover the extensive work on biological membranes. Other related reviews can be found [1–4], as well as other articles in this special edition.

The behaviour of molecular species at the solid-liquid interface is central to a wide range of systems relevant to both academic and commercial uses, including lubrication, corrosion, biomedical implants, renewable energy storage and enhanced oil recovery. In many cases the overall performance is determined by the structure at the interface. NR is able to investigate these adsorbed interfacial structures, non-invasively, *in-situ* and under conditions representative of their commercial use; particularly exploiting the high penetration, surface specific nature of the reflection and the ability to change contrast to observe the species of interest.

The details of the NR technique can be found elsewhere (e.g. [1,5]). In short, the neutron beam impinges onto the interface of interest at low angle,  $\theta$ , as schematically illustrated in Figure 1 and is reflected at the same angle ('specular' reflection). In this geometry the experiment is sensitive to structure normal to the plane of the interface. The beam is usually incident through the solid phase to minimise attenuation. A solid-liquid interface is generally produced by clamping a 'trough' to one side of the solid (Figure 1).

For neutrons, the scattering power does not vary in a systematic fashion with atomic number and different isotopes of the same element can give very different scattering strengths (referred to as the scattering length and the related variable of the scattering length density (SLD)). Most importantly, hydrogen (H) and deuterium (D) can be readily distinguished. By varying the H/D ratio it can be possible to 'contrast match' components so they are not 'seen', all without altering the chemical behaviour of the system. This approach can be used to highlight particular components and/or greatly simplify the structural analysis. For example, it is common to exploit D<sub>2</sub>O to determine the location of water in interfacial structures such as swollen polymer films and surfactant adsorbed phases.

Examples of typical NR data and the relevant SLD profiles are illustrated in Figure 2 with reflected intensity as a function of  $Q_z$ , the momentum transfer perpendicular to the plane of the interface,

$$Q_z = \frac{4\pi}{\lambda} \sin \theta$$

where  $\lambda$ , is the radiation wavelength. Figure 2 shows the critical  $Q$  ( $Q_{\text{crit}}$ ) below which there is total reflection and above which the reflectivity falls quickly. It also shows how a layer at the interface, of thickness  $d$  will produce interference fringes in the data (Kiessig fringes), with the amplitude dependent on the relative contrasts (difference in SLD) and the frequency inversely proportional to the thickness. This is equivalent to the formalisms used in thin film optics. Generally, the experimental data are interpreted by fitting structural models where the interface is considered to be made of a series of layers, each with a thickness, SLD and roughness. There are a number of available codes, including GenX[6], Motofit[7] and Rascal (A. Hughes, ISIS). Where possible, several contrasts are measured and simultaneously fitted to help constrain the fit.

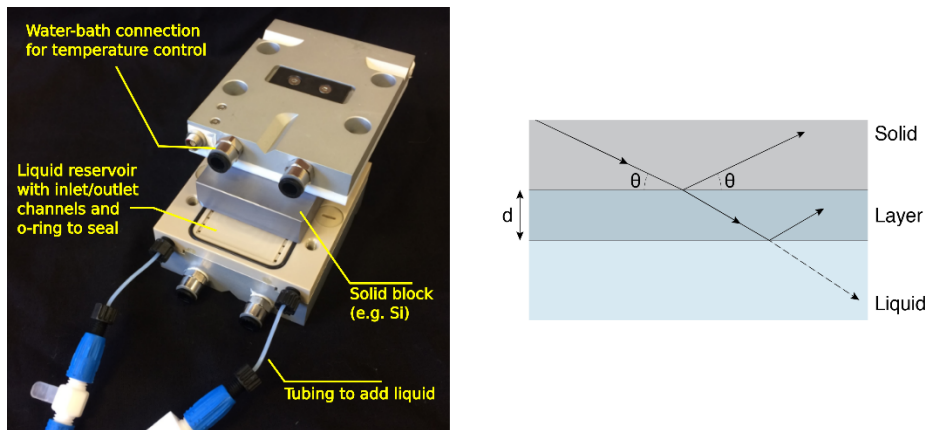


Figure 1: Annotated photograph of a 'typical' solid-liquid cell for NR and a schematic of the specular NR geometry from a solid-liquid interface showing transmission through the solid to the interface, with a surface layer of thickness ' $d$ '.

## 2 Systems of interest

We have broadly divided the material into the following categories: (i) substrates, (ii) liquids and (iii) adsorbed systems, which includes some details on sample environment advances, with the aim to highlight trends and important developments.

### 2.1 Solid Substrates

For studies of the solid-liquid interface, there must be good transmission through the solid substrate, to a highly polished, very flat surface. High transmission generally requires a crystalline substrate to minimise scatter within the block. Therefore, most work uses silicon, sapphire ( $\text{Al}_2\text{O}_3$ ) or quartz – which have the required transparency but different chemistry, with a few studies using natural calcite crystals(e.g.[8]). There is an interesting study of several anionic surfactants on the cationic alumina substrate, where a maximum in the adsorption is observed, which is accounted for using the changing activities of the surfactants and ions.[9]

Substrates can be modified using thermal or chemical treatments for example, to create hydrophobic surfaces. This often involves octadecylsilane (OTS) coated silica, with some

studies using fluorocarbon or hydrophobic polymer treatments e.g [10,11]. The reduction in the density of water at the hydrophobic interface continues to attract interest, along with studies of biomaterials on hydrophobic surfaces arising from challenges of protein storage and delivery and adsorption of surfactants e.g. [10,12]. Work addressing differences in adsorption on ‘hard’ or ‘soft’ hydrophobic surfaces has also been reported.[13]

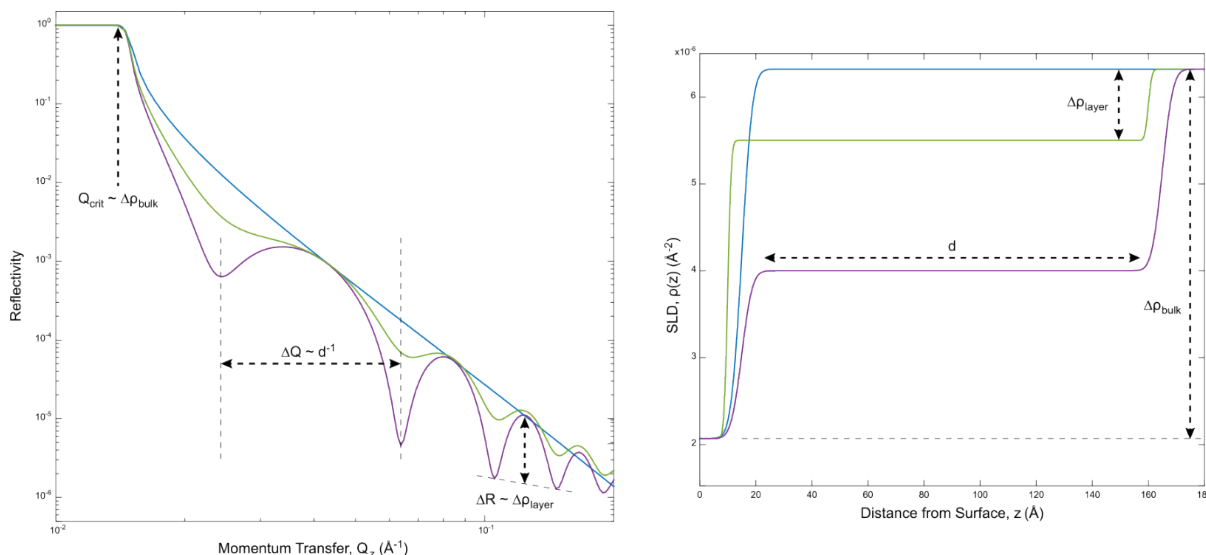


Figure 2: Examples of neutron reflectivity profiles and corresponding scattering length density (SLD) profiles, showing the changes with an adsorbed layer on the surface of thickness ‘d’ and different contrast ( $\Delta\rho_{\text{layer}}$ ). The critical edge ( $Q_{\text{crit}}$ ) is determined by the difference in bulk SLD ( $\Delta\rho_{\text{bulk}}$ ). Blue = Si-D<sub>2</sub>O interface (typical bare solid-liquid); purple = 15nm layer at the solid-liquid interface; green = 15nm layer of lower contrast.

An alternative approach to study surfaces which are not transparent to neutrons, is to support a thin film of the material on a transparent substrate. This has been reported for an increasing number of metal systems including Fe[14,15], Ti[16–18], Cu[19–25], Ni[26–28], Al[29,30] and Au[31–34]. Steel[35] remains a challenge with the overall deposited composition replicated, but the metallurgical aspects are not necessarily typical of bulk steel (see section 2.3 below). Metal films have also been used as magnetic contrast layers for biological studies but will not be covered here.

Other ‘supported thin layer’ systems include mica and graphene. Clay mineral interfaces are important for commercial applications such as enhanced oil recovery. A recent highlight in this area has come with breakthroughs in the study of mica surfaces: by Speranza et al.[36] for x-rays and Browning et al.[37] for neutrons. Interestingly, these non-invasive reflection methods identify different surface structures to those observed by AFM. A variety of studies of adsorption and desorption on mica have recently been presented. A particular highlight has been the role of ions e.g. [38–41].

Surfaces that mimic the properties of hair, skin and fabrics for commercial products have also been addressed.[1,12] Cellulose is a model for cotton or fabrics and bio-diagnostic devices, as well as other functional surfaces which exploit its regular polysaccharide surface and well-defined composition.[12,42,43] It has also been prepared as a perdeuterated film ideal for NR.[44]

## 2.2 Liquids

Unlike the solid component, a wide range of liquids, solutions and dispersions can be used for NR with selection based on particular chemistry, the amount and cost of material

available and the neutron contrast. Perdeuterated solvents and/or additives are often used to provide enhanced contrast. The majority of studies use water and aqueous solutions which are relevant for biomedical, detergency and related applications. There is also substantial interest in non-aqueous systems, relevant to engineering applications in friction, wear and corrosion. In addition, there have been studies into magnetic particle dispersions, as well as more unusual liquid phases.

A number of papers have used colloidal dispersions of magnetic nanoparticles (NP), mainly magnetite, adsorbed on a silicon substrate e.g. [45–47]. The principle interest here is in biomedical applications, such as contrast agents for NMR. A particular attraction of NR is that both the chemical and magnetic structures can be deduced, from both aqueous and non-aqueous solvents.[45,46] In general, they report an adsorbed organic layer of the stabiliser, used to keep the NPs colloidally stable, with a layer of NPs on top. The effects of a magnetic field and shear are also reported.[47]

Liquid crystalline nanoparticles (LCNP), usually made of a polymer stabiliser with lipids and/or surfactants, are particularly attractive for their ability to encapsulate and solubilise other species in drug delivery systems e.g. [48]. Related liquid crystalline phases deposited by spin coating and then rehydrated in contact with water have also been studied, including using off-specular scattering to measure the lateral structure e.g. [49].

The interfacial structural of ionic liquids has been addressed; both the adsorption of pure ionic liquid onto a charged surface, and adsorption of ionic liquid molecules from another solvent e.g. [33,50,51]. These are reported to have good conductivity and lubricating properties due to their layered structure. Their static behaviour has been recently characterised at the oil-silica interface,[50] mica surface[51] and Au electrode surface,[33] with more detail in section 2.3.

Finally, deep eutectic solvents (DES), which have a range of interesting potential applications, have been investigated by NR to determine molecular volumes[52], as well as a solvent for the electrodeposition of Au, Cu and Sn.[31,32]

## **2.3 Adsorbed systems**

This section presents several principle themes evident in the recent literature: electrochemistry, corrosion and metals, polymers and application of extreme conditions, with a focus on the role NR has to play.

### **2.3.1 Electrochemistry**

It is important to measure the electrode-electrolyte interface *in-operando* due to complex time- and potential-dependent behaviour. Techniques such as AFM and QCM-d have been used but are not able to give the same level of structural information that NR can provide for electroactive films, which has long been of interest[53]. For NR, adapted solid-liquid cells are required which enable 2- or 3-electrode configurations for electrochemistry measurements (e.g. CV or EIS), sometimes in combination with other techniques.

There is significant interest in energy storage and battery technology in NR literature. Li-ion batteries (LIBs) have been widely studied due to the unique insight which NR can offer. Light elements (e.g. Li and H) can be difficult to measure by other techniques, but both are readily characterised by NR and exploiting the very different scattering of  $^6\text{Li}$  and  $^7\text{Li}$ . The NR experimental setup can also be optimised to make kinetic measurements accessible on the

NR time-scale (e.g. control of reaction rate using the current density, or stroboscopic measurements if the changes are independent of cycle number) - Figure 3.

A ‘solid electrolyte interphase’, or SEI, layer is reported to form on LIBs affecting the function of the battery, including cyclability and safety. However, the exact layer formation process is unclear and depends on several factors, including electrode, electrolyte, charge-status and cycle number, with this area receiving significant attention and review e.g.[54–56]. Recent studies have investigated several different electrolytes and identified that the first changes are generally seen at open circuit voltage (OCV) with further irreversible changes during the first charging stage. Other, smaller changes are then seen through the rest of the cycling process.

NR has been used to identify a number of characteristics of the SEI including irreversible Li incorporation,[25] formation of a “skin”,[57] the report of a “breathing” mode [24] and the important role of additives[23], with precise details depending on the electrode and electrolyte used. Importantly there are discrepancies between these *in-situ* NR measurements and complementary *ex-situ* XPS data. Significantly, *in-operando* studies (vs. *in-situ* with equilibration), have been reported where the time- and potential-dependence of the SEI can be observed.[57] Figure 3 shows the development of an enriched surface phase, surface layer and deeper lithiation during the first cycle of a Si crystal. This shows the clear contrast between Si and Li (SLD difference), as well as the accessible temporal resolution of the process (in this case 300 s/run).

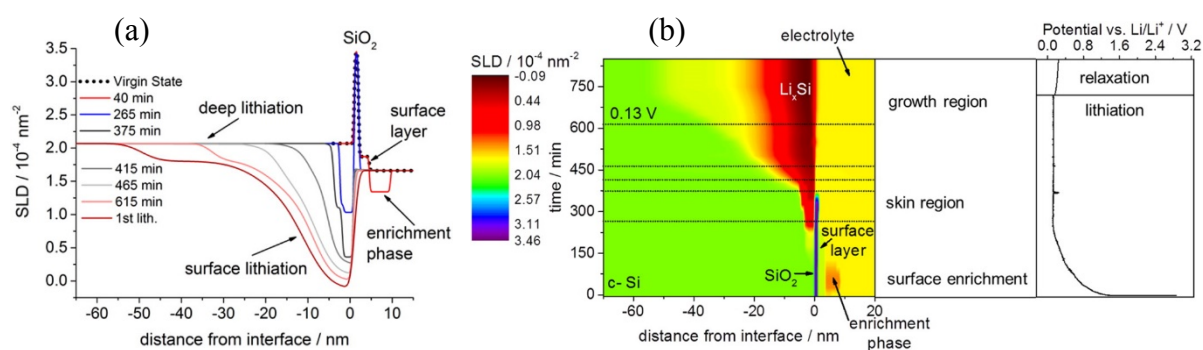


Figure 3: Example changes of the SLD profile for Li incorporation into Si using *in-operando* measurements to show the time dependence, with 300 s/run. (a) shows the SLD progression with time from the virgin state to the end of the first lithiation; (b) colour plot of the same changes, highlighting the composition changes, with the potential of the working electrode vs. Li/Li<sup>+</sup> given on the right hand side. Reprinted with permission from [57]. Copyright (2016) American Chemical Society.]

Kawaura et al.[16] (also *in-operando* approach) reveal the growth of the SEI and composition change onto an amorphous carbon electrode using a time-slicing approach. This complements another study using crystalline C and an interesting combination of NR and AFM.[58] This provides a comparison between localised surface-structure and the structure at greater depth, which enables a growth model to be proposed.

A couple of other interesting electrode surfaces studies look at the plating of Li onto a Cu electrode[22] and the use of an alumina capping layer on Si as a pseudo-SEI.[29] This protects the Si film from the electrolyte, whilst allowing Li inclusion with a pore collapse and regrowth mechanism.

More recently, *in-situ* electrochemistry has been applied to the study of electrodeposition of Ag, Cu and Sn onto Au from a deep eutectic solution.[31,32] This work used fine time-slicing and ‘event mode’ of the NR data (500 s/run in this case) alongside simultaneous thickness electrochemical potential (STEP) and QCM measurements to understand the kinetic behaviour in coating and stripping mono- and bimetallic films. This brings NR onto a similar temporal resolution to the other techniques used in this area and is a likely growth area for future studies.

Specialist electrochemical NR cells are also used for the study of potential-sensitive polymers, which can have a wide range of applications, such as ion-selective electrodes for sensors[59] or organic electronics[34]. In these cases, the data reveal that only thin layers are needed for effective sensors as the reaction only happens in the surface region, and that the swelling of grafted electronic organic films can be controlled with potential.

McCree-Grey et al.[17] have measured the dye in dye-sensitised solar cells in a redox electrolyte under “working conditions” of the cell, although without an applied potential. This highlighted the importance of measuring *in-situ*, with the electrolyte influencing the dye-surface structure. Parker et al.[21] have used an interesting combination of NR, CV, SERS, contact angle and XRR to understand how the adsorption of n-octanohydroxamate on Cu is altered with potential. This is a molecule used in metal ore extraction and corrosion inhibition. This powerful range of techniques allows the authors to link changes in the Cu oxidation state with the enol vs. keto forms of the additive and the passivation of the surface.

Pilkington et al.[33] have used NR to monitor changes in the structure of ionic-liquids (IL) under applied potential. They consider both the pure IL as well as in a solvent mixture, and find a potential-dependent boundary layer of different IL structure at the Au electrode interface.

Supercapacitors are a close-relation to batteries but there have only been a couple of NR studies in this area. Vezvaie et al.[60] measured the structural changes of a  $\text{Co}_3\text{O}_4$  thin-film pseudo-capacitor and found that the whole film changes reversibly with applied potential. The combination of EIS and NR gives contrasting sensitivity to the different parts of the system. They also employed a similar approach to understanding hydrogen incorporation into Ti films, with four distinct regions of the cathodic polarisation process.[18] More recently, Li et al.[26] considered the changes in a  $\text{Ni}/\text{NiO}_x$  film with cycling, which are known to have good supercapacitor stability. Here, they make use of the additional contrast available for magnetic materials using polarised-NR (PNR) and suggest a porous network develops, which alters the capacitance (supported by SEM).

### 2.3.2 Corrosion and Metals

Corrosion is a very expensive industrial problem and there has been a growing number of articles using NR to investigate this, with recent review articles discussing developments in the field e.g. [61,62]. NR has been applied to an increasing range of metal surfaces including Fe,[14,15] Ni,[27,28] Cu,[19] Ti,[18] and steel.[35] In general, the changes in metal films within a corrosive environment are followed, with additives present to protect the film.

Ha et al.[27] have looked at the changes in Ni oxide with potential under alkaline conditions, but with an emphasis on understanding the passive film formation and protection from

corrosion. They also look at whether there is an isotopic effect between  $^1\text{H}$  and  $^2\text{H}$  (D). This is particularly important for NR given the role of H/D substitution in contrast variation. It has been shown that the charge of the additive is important in protected Ni in acidic conditions.[28]

Similar behaviour was observed for Fe in seawater, where the initial surface treatment was also found to be important.[15] Corrosion of materials in oil has also been measured, with the inhibition of Cu from S-based corrosion tested. Interestingly, the additive which forms the most densely packed layer did not provide the best protection, implying that blocking specific surface sites are more important rather than a “blanket” coverage of the surface.[19] In a study of the importance of unsaturation of fatty acid on adsorption from oil, Wood et al.[14] combine the PNR data with SFG and depletion isotherms to understand the structural changes on the Fe surface, again highlighting the use of multiple techniques to address these complex problems. This is not just limited to experimental techniques, with simulations becoming an increasingly important complement to NR.[63]

Polymers can be used to form a barrier film, or protective coating. Payra et al. have used NR to provide structural information of a bioinspired anticorrosion coating, which can be tied to the observed protection.[64] Water penetration is a common theme in this area; Zhou et al. have looked at water penetration into plasma polymerised coatings, using hydrophilic and hydrophobic systems.[65] A combination of NR, SFG, XPS and ATR-FTIR are used to deduce the chemical and physical structure. No water gets through the hydrophobic film to the substrate in the time of the measurements which implies an effective barrier.

The use of NR to study corrosion, although a relatively small field, is an area we believe there can be significant further development.

### **2.3.3 Polymers**

There are a wide variety of experiments exploiting NR to investigate polymers and their behaviour at the solid-liquid interface. The polymer films can be prepared in a variety of ways: spin-coating, grafted ‘brushes’ or layer-by-layer (LbL) deposition, depending on the required architecture and chemistry. Many studies are concerned with responsive polymers, where behaviour is controlled by changing the external conditions: added salt, pH, temperature or pressure. Salt and pH are generally used for charged polymers (polyelectrolytes – PE) and temperature for non-ionic polymers (e.g. [66]). Polymers have been used in combination with electrochemistry (see section 2.3.1 above), pressure and shear (see section 2.3.4 below), as well as for corrosion inhibition (see section 2.3.2 above).

Spin-coated PMMA films are of interest for biocompatible modification of surfaces, due to its suitability use in for humans (e.g. lenses or dentures). They can also be used to support new graphene films, with the PMMA dissolved away during the preparation. However, it has been found using NR that a significant fraction of the PMMA still remains after this process e.g.[67].

Polymer ‘brushes’ of tethered chains are often used as models of colloidal stabilisers or to provide surface modification. NR experiments can be used to establish the segment density distribution on swelling with various solvents, usually exploiting H/D labelling. An interesting application of this is in the capture of Uranium on PE brushes.[68,69] The polymers are generally bound to the surface through covalent interactions, however Tanoue et al.[70] have investigated a di-block co-polymer bound to the surface by adsorption



chemistry of one block, with the other block allowed to penetrate and create the crosslinking. The brush attains a surprisingly high surface density, with the hydration energy of the hydrophilic block supporting the extension of the brush during swelling.

There has also been a great deal of work on layer-by-layer (LbL) deposition of PEs and related materials, including the formation and characterisation of PE multilayers (PEMs), considering chain mobility, inter-diffusion, inclusion of barrier components or ionic strength. Closely related is the preparation of hydrogels in LbL deposited films that are cross-linked after deposition (e.g. [71]).

Some recent work highlighted the combination of responsive PEs with the useful optical properties of nanoparticles (e.g. for sensors).[72,73] These show the strength of H/D contrast variation to extract the locations of the different components, alongside combining x-ray and neutron scattering. Figure 4 shows an example of how the different distributions of polymer and nanoparticles can be determined using NR, with a clear pH dependence on the structure.[72]

Polymers can also be combined with dendrimers and surfactants,(e.g. [74]) enabling some very complex architectures.[75] PEs have been combined with lipids to help understand bio-lubrication in human joints, with additional details given in section 2.3.4 below.[76,77] It has also been shown that polystyrene particles can be ‘glued’ onto a silica surface (both negatively charged) using adsorption of an albumin protein (cationic polymer).[78]

Rotaxanes are formed when a ring molecule threads onto a linear molecule and is held in place with ‘stoppers’ on the chain with potential applications including host-guest complexes or protein binding control. Due to the low volume fraction of material, these can be challenging to measure using NR but there have been a few studies e.g. [79,80]. This includes threading a cyclodextrin (CD) onto PNIPAM to form a pseudorotaxane (no ‘stoppers’), with CD binding causing extension of the polymer.

Although most work considers aqueous systems, there has been significant work using CO<sub>2</sub> to swell polymers, particularly in the supercritical regime where there are large density fluctuations that lead to significant uptake even for CO<sub>2</sub>-phobic polymers (e.g. [81,82]).

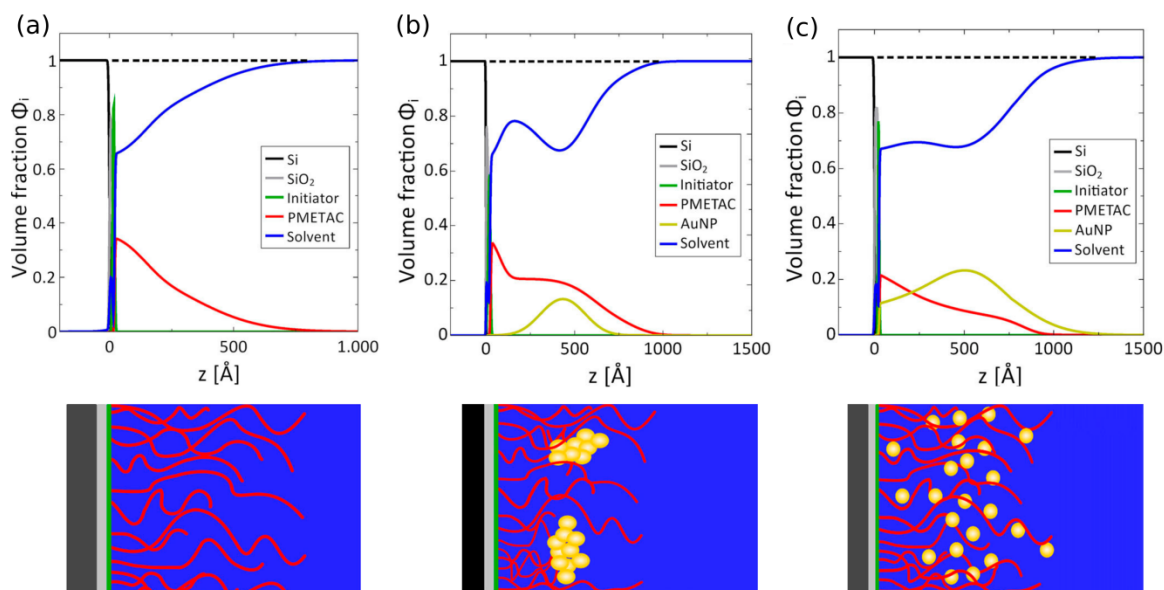


Figure 4: The distribution of polymer and Au nanoparticles (AuNP) on Si substrates determined by NR, with a schematic of each system given below. (a) neat PMETAC brush; (b) PMETAC brush with AuNP at pH4; (c) PMETAC brush with AuNP at pH8. This is adapted from Boyaciyan et al.[72], with permission of AIP Publishing.

### 2.3.4 Extreme conditions

“Extreme conditions” generally encompasses working under particularly high, or low, pressure, temperature or shear conditions, often relevant to industrial or biological environments. The application of extreme conditions has been of interest for a significant length of time, with early work considering shear using flow cells[83,84] and applying pressure through SFA-type equipment[85]. Improvements in NR (instrumentation, flux and data analysis) have allowed significant progress to be made in sample environment development in order to measure *in-situ* under these conditions. This is an exciting area of growth, with many future opportunities.

In order to apply high pressures, a couple of approaches have been used. Hirayama et al. use Ar gas introduced into a liquid reservoir to control the pressure of a lubricant additive mixture against a Cu surface.[20] This is a similar approach to work of Koga et al. looking at swelling of polymers using supercritical CO<sub>2</sub>, (section 2.3.3 above).[81,82] One limitation of this approach is the purity and solubility of the gas used.

To overcome this, Kreuzer et al. designed a hydrostatic cell which keeps the sample liquid and the pressurising fluid separate, via a separation piston cell, up to 1 kbar and 60°C. More recently, this cell has been used in an interesting study looking at the antagonistic relationship of pressure and temperature on polymer brush structure.[86] Within this work, they use a combination of NR measurements and DFT theory to hypothesise a general relationship for the P-T effects on hydrophobically associated homopolymers at pressures <1 kbar. They find that ~100 bar can be considered equivalent to 1 K temperature rise (see Figure 5). They have preliminary results suggesting that hydrophilic polymers that show little change with temperature, also show little change under these pressures.

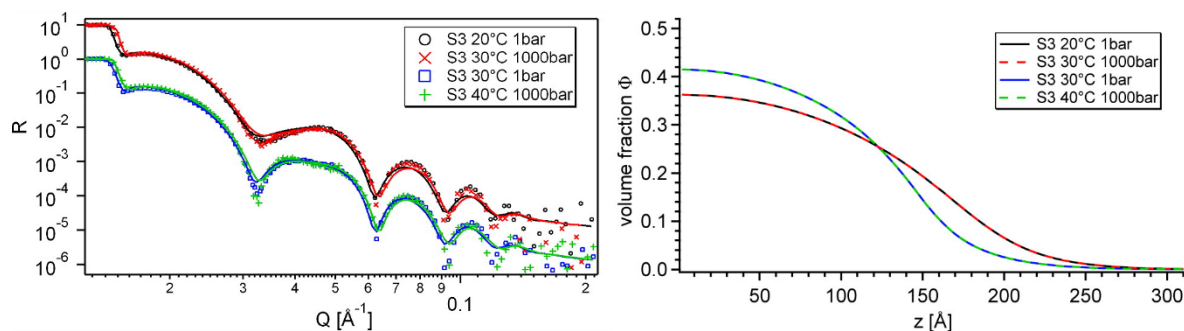


Figure 5: NR data with fits for a grafted PDMAEMA brush as a function of temperature and pressure, alongside the volume fraction profiles of the polymer associated with these fits. The data for 30°C, 1000 bar and 20°C, 1 bar match, as do the 40°C, 1000 bar and 30°C, 1 bar, showing the 1000 bar/10 K equivalence effect. Reprinted with permission from [86]. Copyright (2013) American Chemical Society.

The main limitation of this pressure cell is the large solution reservoir and limit of  $\sim 1$  kbar. A further development of Jeworrek et al. has enabled pressures up to 2.5 kbar using only small volumes of solution. The pressurising and sample fluids are separated by a thin polymer membrane, which has enabled the study of a biological system, where large sample volumes are often prohibitive.[87] The effect of pressure on an enzyme in a polyelectrolyte brush environment up to 2 kbar is investigated with NR used to measure the structural changes, ATR-FTIR to determine changes in the secondary structure of the enzyme and fluorescence to show the enzymatic activity. This combines to give a thermodynamic model for the changes based on activation volumes.

Elevated pressure is particularly relevant for industrial applications and Junghans et al. have used NR to improve understanding in the corrosion of Al for deep-sea infrastructure.[30] By applying 0.6 kbar to a saline solution, they observe changes in the passive layer on an Al film towards a more hydrated form, which is thought to be more susceptible to localised corrosion.

Adsorption can also be affected by physical confinement as measured by surface force apparatus or atomic force microscopy, relevant for boundary lubrication and tribological contacts. This buried structure is incredibly difficult to directly measure by other methods, however, it is also non-trivial to achieve close confinement over the area required for NR. A recent review, has considered this in more detail,[88] so only the most recent work since will be covered here. Most of the measurements have measured the confinement effects on polymeric layers using specialist cells. One approach by the group of Richardson is to use a flexible Melinex® sheet as the opposing surface in a parallel-plate geometry. This flexibility allows accommodation of any waviness or entrained dust. They are able to control the interpenetration of two polymer brushes with either no charge or asymmetric charge by altering the pH.[89]

An alternative method to confine polymers used two coated interfaces separated by a thin, controllable layer of water, which has been applied to the solid-water and the air-water interfaces[90,91]. The water layer thickness was controlled using relative humidity. The data presented showed decreasing thickness of the interacting-brush region with dehydration (increasing confinement), for both neutral and polyelectrolyte brushes.

The effect of lower pressures (up to 0.45 bar) on the adhesion between a polymer brush and a PE gel has also been measured, with NR providing information on the structure of the two components and what happens when this interface fails. The thickness of the brush is found to have a significant effect.[92]

When considering extreme conditions of boundary lubrication, both pressure and shear are significant. Ideally, studies under shear would also be *in-situ* due to the non-equilibrium nature of these conditions. One of the more straightforward experimental setups for this is to use an in-line pump to create Poiseuille flow within the solid-liquid cell. However, care is needed to optimise the surface shear stresses and avoid pulsed flow. Singh et al. used a custom laminar flow cell to measure changes in layered polymeric systems under shear rates of  $\sim 53000\text{s}^{-1}$ . [93] They see some loss of water with shear rate and some dependence on pH, which are explained through an osmotic pressure model. Lower shear rates of  $\sim 300\text{s}^{-1}$  have been applied to layers of magnetic nanoparticles (NPs). [47] Here they find a static layer of NPs on the surface with a depletion layer to the moving ferrofluid above, which is not seen in the static case.

One can also apply shear using a rheometer *in-operando* giving simultaneous measurement of the bulk rheology and surface structure. Generally, the NR substrate is the plate in a “cone-plate” geometry, which provides a constant shear rate over the neutron footprint (rheo-NR). This has recently been applied to polymer brushes of varying length and grafting density. [94] They find a reversible collapse of the brushes with shear, which is dependent on shear rate. This is combined with coarse-grained computer simulations to further understand the observed changes, which are predominantly in the brush-bulk region rather than the inner brush. The simulation is able to identify slight deformation and tilt of the polymer, which is not possible in the NR measurement – another example of the strength in combining techniques.

Although the application of shear has been dominated by polymer systems, Welbourn et al. have applied rheo-NR to a multi-layered surfactant system. [95] Under the shear rates applied, the ordered outer bilayers are removed from the surface, with the layer closest to the substrate remaining. This is dependent on the type of shear applied, with complete loss of the surfactant multilayers dependent on strain amplitude for steady shear and incomplete loss under oscillatory fields.

Surface-active lipid linings as mimics for cartilage coatings [77] are another multi-layered systems, which shows shear-dependent changes and a “buckling-like deformation”. This very interesting paper uses a complex, custom setup combining shear with *in-situ* NR and ATR-FTIR, to understand lubrication in mammalian joints. By comparing the lipid behaviour with and without a hyaluronic acid analogue they are able to highlight structural (NR) and chemical (FTIR) changes, which improves understanding of these important systems.

Temperature is an important control parameter affecting adsorption and surface structure. Relatively modest elevations in temperature have been investigated for some time and there are several examples above. However, many engineering applications require access to much higher temperatures, which creates technical challenges over sample cell design. Therefore, to date, most of the extreme high (or low) temperature NR studies have focussed on the solid-air interface while several studies have used pressure to assess changes under related extreme conditions. Hence we identify that this is an area for future development.

### 3 Summary

It is clear that neutron reflectometry studies of the solid-liquid interface are in fine health, although we are only able to give representative examples here. Recent developments in this area cover a very wide range of topics: particularly an increased range of substrates (e.g. metals and minerals) and liquids, solutions and dispersions, with key themes emerging in

electrochemistry (batteries and supercapacitors), corrosion, polymers and increasing application of extreme conditions. NR is providing information about these systems that is unobtainable by other means, and, when combined with complementary experimental and simulation techniques this can provide substantial insight. The simulation results can greatly improve detailed understanding of these systems and aid in data analysis. In a growing number of cases, novel sample environments are being developed which allow simultaneous complementary measurements. We believe that these developments are likely to continue, opening up an even wider range of possibilities.

The expected future upgrades to neutron sources and instrumentation is likely to enable faster measurements and/or smaller samples for NR. This is already seen in some of the time-dependent studies discussed above. With these improvements, we see the ability to measure smaller samples as a particularly important development, which will open up science fields which are currently unobtainable. This is particularly the case with more ‘industrial’ samples, where it may be difficult to deposit films of larger size, or where the liquids used are particularly precious. The expected increase in temporal resolution will also be important in providing further insight into structural changes at the solid-liquid interface; enabling greater information to be gathered from dynamic systems of applied potential, pressure and shear. We also look forward to seeing how, as yet untested (or unknown), opportunities will unfold with NR.

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